



Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at <http://about.jstor.org/participate-jstor/individuals/early-journal-content>.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact support@jstor.org.

tro-telescope (prism edge) on its axis until the inclinations also coincide. In reality the phenomenon is more complicated as the spectrum fringes change both size and inclination on rotation of the spectrum. In case of the completion of this twofold adjustment the slit of the collimator may be made indefinitely wide or removed altogether (undesirable light is to be screened off). The spectrum fringes may thus be given any intensity of illumination at pleasure, while the wave length corresponding to any fringe may be found by narrowing the slit until the Fraunhofer lines reappear. When the fringes are small the orientation of the spectro-telescope revolving around its axis may be determined by the appearance and evanescence of fringes. On the other hand the spectro-fringes, particularly if large, remain clearly enough in the field for the observation of the motion of a large number (i.e., for interferometry), before they vanish.

Similar results were obtained in broadening the vertical string of interference beads of reversed spectra. An account of these experiments will have to be omitted here, as they are much more complicated.

AN ELECTROMAGNETIC HYPOTHESIS OF THE KINETICS OF HETEROGENEOUS EQUILIBRIUM, AND OF THE STRUCTURE OF LIQUIDS

BY WILLIAM D. HARKINS

KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO

Communicated by J. Stieglitz, March 24, 1919

While Gibbs,¹ in his remarkable treatise "On the Equilibrium of Heterogeneous Substances" has given a very broad treatment of his subject from the thermodynamic standpoint, nothing is included which would give any idea of the probable distribution of a component between a set of phases from a knowledge of the properties of only the pure component and of those of the phases before any of this component has been added to them. It is the purpose of this paper to indicate that the general nature of such a distribution can be predicted in most cases from the standpoint of the hypothesis that it is determined mainly by the intensity and nature of the electromagnetic field surrounding the molecules, and by the motion of the molecules and atoms. There is considerable evidence that the atom consists of a positively charged nucleus surrounded by a system of negative electrons. On such a basis it is to be expected that the atom, and therefore the molecule, would be surrounded by an electrostatic field. Inasmuch as there is much evidence from the magnetic properties of substances that the electrons are in motion, this is also to be considered as a magnetic field. Such a composite field is usually said to be electromagnetic.²

That the application of this hypothesis is not a single problem, is indicated by the electrical duality of such a field, and by the fact that while a part of the combinations between atoms or molecules in such a system may be of the nature of primary valence unions,—presumably a fitting of one or more of the outer electrons of one atom into the electronic system of another atom,—other molecules may be grouped together, though very much less firmly, by forces which still remain after all of the primary valence combinations have been made. In this preliminary paper only the more general features of the hypothesis will be considered,—that is only those which can be treated on the basis of a general knowledge of the intensity of the electromagnetic field around the molecule. The greatest obstacle in this connection is the meagerness of our knowledge of the characteristics of this field, which in this paper will be designated as the *stray field* of the molecule, since it gets out beyond the electronic constituents of the molecule.

The first problem which will be considered is: given two components (A) and (B), each in a phase by itself and both phases in the liquid state at the common temperature (T), when will these two phases be miscible and when will they be practically insoluble in each other? The relation is not difficult to find, for we know that (A) mixes with itself; so perfect miscibility should result when the stray fields around the molecules of (B) are sufficiently like those around the molecules of (A). Likeness of the fields in this sense means likeness in intensity, and presumably in the rate at which this intensity falls off with the distance from the molecule. A sufficient likeness of stray fields is also the condition which must hold if Raoult's law

$$p_A = P_A \frac{N_A}{N_A + N_B} = P_A x_A, \quad p_B = P_B \frac{N_B}{N_A + N_B} = P_B x_B$$

is to be valid. Here p_A and p_B are the vapor pressures of (A) and (B) in the mixture, P_A and P_B are the vapor pressures of the pure liquids, and x_A and x_B are the mol fractions in the mixture. If (A) is a liquid, but the state of (B) is unknown, then (B) is apt to be a liquid if the pressures and temperatures of both are the same, though the size of the molecule is a factor which also has an effect. If the stray fields around the molecules of (A) and (B) are sufficiently different, then the two substances will be practically insoluble in each other—if the difference is extreme, one of the substances will be a gas and the other a solid, if they are at ordinary room temperatures.

Since the intensity of the stray field falls off more rapidly with the distance in the case of some molecules than with others (it probably decreases more rapidly around small *atoms* than around large atoms), it is not possible to give a list arranged in the order of increasing intensity of the stray field which is correct in all respects. Thus, while the intensity of the field close to the atoms of the heavy metals is very high, it undoubtedly decreases rapidly with the distance. On the other hand there are facts which seem to indicate

that the forces around the oxygen or nitrogen atoms of organic compounds or of water, or such atoms as are commonly called 'polar,' extend to a greater distance, although their intensity is less at the ordinary atomic distances. However, the following list may be considered to give something of this order of increasing intensity for a limited number of substances. This list has been obtained for the most part from a consideration of the *surface tension relations* of substances, and is as follows, beginning with those substances around whose molecules the stray field is weakest: helium, neon, hydrogen (molecular, not atomic), argon, krypton, xenon, nitrogen, oxygen, methane, carbon monoxide, and the following organic compounds—saturated aliphatic hydrocarbons, aromatic hydrocarbons, sulphides, mercaptans, halogen derivatives (methyl chloride, carbon tetrachloride, chloroform, and ethylene chloride, with rapidly increasing fields), unsaturated hydrocarbons, ethers, esters, nitro compounds, nitriles, aldehydes, ketones, alcohols, amines, acids, and unsaturated acids. Following these are water, molten salts, heavy metals, boron, and carbon. The list of organic substances is arranged for derivatives with short hydrocarbon chains. A lengthening of the chain causes a displacement in the direction of lower intensity for polar derivatives, but probably toward higher intensity in the case of the hydrocarbons themselves. It will be seen that in general the greater the distance between the substances in this list, the less their solubility in each other, the closer together, the more soluble. For organic substances, though the present list is much more extensive, it is in agreement with that found by Rothmund from solubility data.³ It is well known that metals in general give concentrated solutions only with metals, carbon, and other similar substances; molten salts dissolve salts or water; pairs of organic liquids are miscible unless the members of the pair lie at the very opposite extreme of the list of organic substances; water dissolves salts or organic substances which are close to it in the list. An interesting illustration of this relation is given by data on the organic halogen derivatives listed above. The solubility of carbon tetrachloride per 100 grams of water is 0.80 grams, while that of chloroform, which lies closer to water, is 0.822 grams; and methylene chloride, approaching water still more closely, has a solubility of 2.00 grams. This is also the order of increasing hydrogen content of the molecule, but that this is not the determining factor is indicated by the fact that methyl chloride and methane, similar compounds containing still more hydrogen, are much less soluble in water. In organic compounds the intensity of the stray field is much higher adjacent to what are commonly called double bonds, than it is near single bonds, and this intensity grows much larger still if triple bonds are introduced. Corresponding to this the solubility of ethane, with its single bond between two carbon atoms, is 0.0507 volumes of gas per volume of liquid; that of ethylene with its double bond is 0.1311, or more than twice as great; while acetylene with its triple bond has a solubility of 1.105, or about 22 times more than that of the single bonded compound.

The above list, giving the order of intensity of the stray electromagnetic fields, will be seen to give the substances in increasing order of cohesion. The atoms or molecules giving the lowest cohesion, such as He, Ne, A, Kr, Xe, etc., are just those which, according to the valence theory of G. N. Lewis (*J. Amer. Chem. Soc.*, **38**, 1916, (762-85)) have *complete* outer shells of electrons (2 for He, 8 for Ne and A). The substances with the highest cohesion, such as carbon, silicon, iron and cobalt, ruthenium, and tungsten and osmium, are elements which lie in the periodic system exactly half way between the elements of lowest cohesion, so high cohesion may be said to result when the outer shell of electrons is half filled or half complete. In other words a low stray field is found when according to the theory of Lewis the atomic or molecular outer shell of electrons is complete, the highest stray field, when the shell is half filled, that is when there is the possibility of the greatest number of electronic linkages directly between the atoms, without the intermediate formation of molecules of a simple type containing only a few atoms. Accompanying a high field the substance is found to have a low atomic volume, a high cohesion, melting point, a low coefficient of expansion, a low compressibility, etc. When the field is low in intensity, the properties are just the opposite.

In analyzing a solubility problem it is well to consider the attraction between the molecules of (A), between those of (B), and also that between (A) and (B). Consider octane and water which are mutually insoluble. It has sometimes been considered that this insolubility is due to the fact that water molecules attract each other more than they do molecules of octane, and that octane molecules attract each other more than they do molecules of water. Now the work of this laboratory shows that while the molecules of water do attract each other much more than those of octane, on the other hand the molecules of octane attract those of water very slightly more than they do those of octane. The much greater attraction of the water molecules for each other is a sufficient cause to produce immiscibility, since it is only necessary that when a group of water molecules is once formed, the mutual attraction shall be great enough to cause the molecules of water to leave the group less often than they enter it, so long as there is an appreciable quantity of water in the octane. The octane molecules are thus left in a phase by themselves.

Since an increase in the intensity of the stray field around the molecule is accompanied by an increase in molecular attraction, it causes an increase in the cohesion of the liquid or of the solid, so in its application to pure liquids the above theory gives predictions which are similar to those obtained by that of Hildebrand,⁴ that liquids of like cohesions are miscible, while those whose cohesions are very unlike are practically insoluble in each other. However, solubility is a molecular scale phenomenon, so there are certain advantages of a molecular theory of the phenomenon. Moreover, the theory presented

here has a much wider range of application, since it may be used to indicate the internal structure of a liquid, to predict the distribution (partition and adsorption) of components between different phases, interfaces, and surfaces (these will be designated by the term *regions*), and is of great importance in theories of ideal and non-ideal solutions:—in other words it is a theory of what is called by Washburn⁵ the '*thermodynamic environment*.' This in the sense of our theory would be designated as the *electromagnetic environment*.

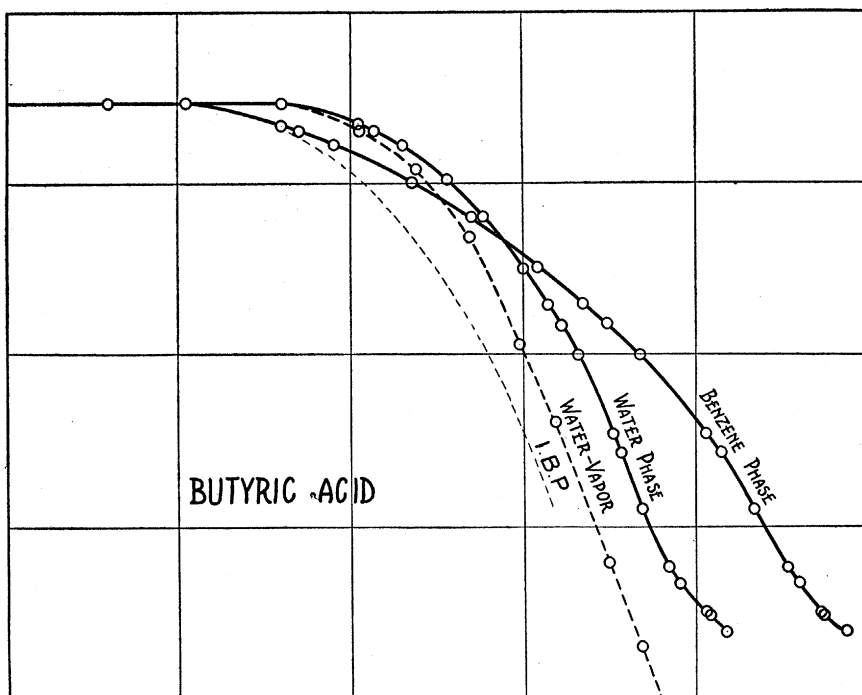
Application to Interfaces and to Distribution between Regions.—While in applying the hypothesis, the intensity of the stray fields around the molecules is of primary importance, at least one additional principle must be used if the direction which any change will take by itself is to be predicted. As might be expected the second law of thermodynamics is of fundamental importance in this connection, and for this purpose it may be stated in the form: Any change which takes place by itself in a system will proceed in the direction which will result in a decrease in the free energy of the system. Thus a surface will decrease in area by itself, but will not increase. Since a rapid variation of the intensity of the stray field with the distance in any direction, is accompanied by a high concentration of free energy, the second law indicates that in any change which takes place by itself, the variation in the stray field becomes less abrupt. If we imagine the surface of a liquid up to a bounding, surface plane, to have just the same structure as the interior of the liquid, then the actual surface always has a smaller free energy⁶ than would be given by calculation for this imaginary surface, and therefore the drop in intensity of the stray electromagnetic field at the actual surface is always less than it would be at a surface of the structure of the imaginary surface. Since a molecule is often made up of several species of atoms, the stray field around it is often unsymmetrical. Thus many organic molecules, such as the primary normal alcohols, acids, amines, nitro compounds, nitriles, ethylene and acetylene derivatives, etc., consist of a paraffin chain around which the stray field has a relatively low intensity (a so-called non-polar group), while at the other end of the molecule there is a group containing oxygen or nitrogen, sometimes with metals in addition, around which the intensity of the stray field is relatively high (a polar group). Such molecules may be designated as *polar-nonpolar*, and designated by the symbol $o\text{---}$, where o represents the polar, and --- the nonpolar end of the molecule. If molecules of this type, such as butyric acid (C_3H_7COOH), are put in a two phase system consisting of a polar liquid such as water, and a nonpolar liquid such as octane, then the free energy of the interface will be less when the transition from one liquid to the other is made by molecules of butyric acid, with their polar ends turned toward the water, and their nonpolar ends turned toward the octane, since in this way the abruptness of the transition is decreased.

The problem here arises as to the distribution of molecules of the polar-nonpolar type between the two liquid phases, their surfaces, and the interface

between them. It may be considered that each region (phase, surface, or interface) exerts a certain restraining force upon (has affinity for) the solute molecules. Since at equilibrium the thermodynamic potential of the solute is the same in all of the regions, it may be considered that the concentration of the solute (at equilibrium) in each phase, interface or surface, gives an index of the restraining force exerted by that region upon the solute molecules. Let us now assume that we have a number of exactly similar two phase systems, each of which consists of equal volumes of a polar liquid, such as water, and a nonpolar liquid such as octane, with an interface of a definite area between them, and into each of these systems we put N molecules of the polar-nonpolar type o—. The hypothesis indicates that with a given polar group the distribution of the N molecules will vary in such a way that with an increase in the length of the nonpolar part of the molecule, the number of molecules, and therefore the restraining force in the octane will increase, while in the water both of these will decrease. The reverse of this occurs when with a given nonpolar chain, there is an increase in the number of polar groups. The greatest restraining force would be exerted on such molecules when they are in the interface, where the nonpolar end of the molecules could turn toward the nonpolar liquid, and the polar end toward the polar liquid. Since the restraining force is greatest at the interface, the concentration in this region should also be the greatest, which agrees with the facts as found by experiment.

In the preceding paragraph it was assumed that the water is completely covered by the octane. Let us now assume that the water has a surface, or a water-vapor interface as well, and that benzene is the nonpolar (slightly polar) liquid. At the water-vapor interface at ordinary temperatures, the drop in average intensity between the stray field in the water and that in the dilute vapor (in which the intensity is practically zero), is much greater than that between water and benzene, so the restraining force on molecules of the polar-nonpolar type should be much greater at the former interface. In complete agreement with this idea experimental tests indicate that *the restraining force is about three times greater at the water-vapor interface than at the water-benzene interface*, when butyric acid is the solute, and somewhat similar results are obtained when the solute is acetic acid. The experimental work was carried out in 1913 by E. C. Humphrey, and was afterward repeated and made more precise by H. H. King and H. McLaughlin. The above results may be expressed in other words as follows: the thermodynamic potential of butyric acid is about three times as great in the water-benzene interface as it is in a water surface, when the concentration of the butyric acid in both of these interfaces is the same, or the drop in mechanical potential which a molecule of butyric acid undergoes in passing from water into the interface is much greater when the second phase is a dilute vapor than it is when the second phase is a nonpolar liquid. This is an illustration of a general case,

and similar relations hold for any molecule of the polar-nonpolar type with reference to the pair of interfaces, polar liquid-vapor, and polar liquid-less polar liquid. Similar work is now in progress, a metal being used as one of the phases, and vapor, water, or an organic liquid as the other. The results of this work are very interesting, but space is wanting for their discussion. They indicate that, corresponding to the greater drop in intensity of the stray field between metal and vapor, in comparison with that between water and vapor, the adsorption at the metallic surface is much greater than that at a water surface for the same concentration of the adsorbed component in the nonmetallic phase.



A striking result obtained was that the number of molecules per square centimeter in the 'constant concentration' film between water and benzene was found to be 2.79×10^{14} , while that between water and air was found to contain 2.77×10^{14} molecules, showing that the number of molecules in such a film is independent of the presence of the second liquid phase, and therefore depends only on the dimensions of the molecules.

These results were obtained by the drop weight and capillary height methods for determining surface tension, as they have been developed in this laboratory.⁷ For such work a high degree of precision is essential. The results for butyric acid are presented in a graphic form in Figure 1, where

the ordinates give the surface tension; the abscissae, the logarithm of the concentration, and the adsorption is obtained from the slope of the respective curve by means of the Gibbs equation, $\mu = \frac{1}{iRT} \frac{d\gamma}{d \ln c}$ where μ is the adsorption, γ is the surface tension, and c is the concentration of the solute. The curve for the water-vapor interface lies to the left of that for the water phase of the two phase system, which indicates that the restraining force of the former interface is the higher. The curve marked I. B. P. represents that which would be obtained for the benzene of the two phase system if the butyric acid in this phase were not associated. The horizontal distance between this curve and that for the actual benzene phase is a measure of the degree of association.

When applied to the structure of a liquid our hypothesis indicates that when the molecules are not wholly symmetrical, there will be more or less grouping of the parts of the molecules around which the stray field is the most intense, the extent of the grouping being a function of the temperature also. It is probable that liquids of this class have more, but a less definite, structure than is commonly supposed. If molecules of the polar-nonpolar type are dissolved in a nonpolar liquid this grouping is commonly spoken of as association of the solute; in a polar solvent it is considered as the solvation or hydration of the solute, in pure liquids it is designated as the association of the liquid. These groupings are constantly being modified by the kinetic agitation, the other factors being the intensity of the stray field, and the space available for the grouping.

A discussion of electrical theories of surface phenomena will be found in papers by Hardy,⁸ Langmuir,⁹ Harkins, Brown, and Davies,¹⁰ Harkins, Davies and Clark,¹¹ and by Frenkel.¹² The present paper will be published in a much more complete form in the Journal of the American Chemical Society, in which there will be taken up the question of what is known as specific adsorption.

¹ Gibbs, *Trans. Conn. Acad., New Haven*, Oct. 1875–May 1876, (108–248), and May 1877–July 1878, (343–524).

² Lewis, Wm. Mc., *Phil. Mag., London*, **28**, 1914, (104–16).

³ Rothmund, *Loslichkeit und Loslichkeitsbeeinflussung*, Leipzig, 1907, p. 118.

⁴ Hildebrand, *J. Amer. Chem. Soc., Easton, Pa.*, **38**, 1916, (1452–73).

⁵ Washburn, *Physical Chemistry*, Chapter XIII, pp. 134–42, also pp. 143, 224, 273.

⁶ Harkins, Davies, and Clark, *J. Am. Chem. Soc.*, **39**, 1917, (553–70, 594–5).

⁷ Harkins and Humphrey, *Ibid.*, **38**, 1916, (228–46); Harkins and Brown, *Ibid.*, **38**, 1916, (246–52), and April 1919.

⁸ Hardy, *London, Proc. Roy. Soc., B*, **86**, 1911–12, (634).

⁹ Langmuir, *J. Amer. Chem. Soc.*, **39**, 1917, (1848–1906); these PROCEEDINGS, **3**, 1917, (251–7). Abstract in *Met. Chem. Eng.* **15**, 1916, (468).

¹⁰ Harkins, Brown, and Davies, *Ibid.*, **39**, 1917, (354–64).

¹¹ Harkins, Davies, and Clark, loc. cit., 1917, (541–96).

¹² Frenkel, *Phil. Mag., London*, **33**, 1917, (297–322).